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ABSTRACT

A 730 kW (2.5×10^6 Btu/hr) firetube package boiler was used to demonstrate the application of reburning for NO_X emission control. An overall reduction of 50 percent from an uncontrolled NO_X emission of 200 ppm was realized by diverting 15 percent of the total boiler load to a natural-gas-fired second stage burner. Tests indicate that the overall reaction order of destruction with respect to initial NO_X is greater than one; thus, larger reductions can be expected from reburning applications to systems with higher initial NO_X. Rich zone stoichiometry has been identified as the dominant process variable. Primary zone stoichiometry and rich zone residence time are parameters that can be adjusted to maximize NO_X reduction.

Reburning applied to firetube package boilers requires minimal facility modification. Natural gas would appear to be an ideal reburning fuel as nitrogen in the reburning fuel has been shown to inhibit NO_X reduction.

INTRODUCTION

Nitrogen oxides (NO_x) emitted from stationary combustion sources have been identified as significant contributors to the degradation of air quality. Modification of the conventional combustion process to reduce NO_x formation in flames by reducing peak temperatures and maximizing fuel rich residence times has proven to be a commercially viable method of controlling NO_x emissions [1]. However, when combustion process modification is impractical or insufficient to meet an emission level requirement, it may be necessary to reduce NO_x from the products of combustion. Reburning, a term coined by Wendt et al. [2] to describe the process of NO_x reduction by injection of a secondary fuel stream, represents an in-furnace NO_x control technology that destroys NO_x formed in the primary combustion flame. Laboratory studies utilizing both flat-flame burners [2] and tubular reactors [3] provided initial evidence of NO_x reduction via hydrocarbon radicals.

In the burning of a hydrocarbon fuel in air, NO_x is formed either from molecular nitrogen (N_2) in the combustion air or from fuel-bound nitrogen. Equilibrium calculations indicating thermodynamically favored speciation at specified temperature, pressure, and elemental constituency predict exceptionally low total fixed nitrogen (non-N_2 nitrogenous species) concentrations under fuel rich conditions [4]. In fuel lean flames, equilibrium NO_x values are extremely temperature sensitive. At typical flame temperatures, equilibrium NO_x levels can exceed 1000 ppm, whereas at typical boiler stack temperatures, equilibrium NO_x concentrations are well below 1 ppm. However, because the kinetics which dictate the speed at which equilibrium is approached are slow, actual NO_x emission levels vary enormously from equilibrium predictions.

There are two key factors associated with the reburning process. First, injection of secondary fuel creates a fuel-rich environment where the chemical driving force is shifted toward N_2 formation rather than oxidation to NO_x. The second key factor is that formation of hydrocarbon radicals from the secondary fuel provides a rapid chemical reaction pathway for approaching the equilibrium state. Figure 1 (taken from [4]) describes the overall chemical mechanism for NO_x destruction by secondary hydrocarbon injection. The key steps include initial nitric oxide (NO) destruction by reaction with the methylidyne radical (CH) to form hydrogen cyanide (HCN). Subsequent reactions lead to ammonia (or NH_i radicals) and eventually to the formation of N_2. Any fixed nitrogen species which exit the fuel-rich zone are partially converted to NO_x upon final air addition.

Though the basic concepts associated with reburning chemistry are not new, development of the technology has occurred only recently. In 1981, investigators for Mitsubishi Heavy Industries (MHI) reported that application of the reburning technology MACT (Mitsubishi Advanced Combustion Technology) to full scale boilers resulted in NO_x reductions of 50 percent, roughly independent of fuel type and initial burner NO_x production [5]. Based on MHI claims, the United States Environmental Protection Agency (EPA), the Electric Power Research Institute (EPRI), and the Gas Research Institute (GRI) have

initiated a multi-scale research and development program to better understand the chemical and physical processes associated with reburning.

As a part of this program, the EPA is conducting in-house studies to investigate the application of reburning to firetube package boilers. Tests performed on a pilot scale package boiler simulator (PBS) equipped with a low-NO_x research burner have entailed extensive modification of boiler hardware and boiler operating conditions to provide fundamental insight into the chemistry and physics of natural gas reburning (as reported in [6]). A series of experiments were then performed on a commercial firetube package boiler to determine the representativeness of results obtained from the PBS tests and to assess the practicality of an actual retrofit application. These application tests are the subject of this paper.

EXPERIMENTAL APPROACH

In a conventional boiler, fuel and combustion air are introduced coaxially through a burner (or burner set) located on the front firing face. With reburning, portions of the fuel and combustion air are diverted from the main burner(s) for injection into the boiler at selected downstream locations. In this way, the boiler radiant section is divided stoichiometrically into three zones: a fuel lean primary zone, a fuel rich reburning zone, and a fuel lean burnout zone.

A North American scotch-type package boiler was used for reburning application tests. The three-pass boiler, 0.61 m (2 ft) in internal diameter and 3.0 m (10 ft) long, has a continuous service rating of 1089 kg (2400 lb) of steam per hour. The North American swirl burner is capable of firing gas, light oil, and heavy oil and has a maximum rating of 733 kW (2.5×10^6 Btu/hr). The mechanical linkage for automatic control of air/fuel ratio with variation in load was disconnected from the burner and replaced with a manual adjustment that permitted independent control of primary flame excess air at any desired load.

Reburning fuel and burnout air are injected into the boiler through a boom assembly inserted from the rear of the boiler down the firetube centerline. The boiler endplate, which provides access for maintenance, was modified with a 9.0 cm (3.5 in) opening to allow for boom assembly insertion. The assembly consists of two telescoping booms, allowing for independent variation in the location of secondary fuel injection and the rich zone length. The inner boom provides for radial injection of secondary natural gas plumbed directly from a 1.36 MPa (5 psi) supply line, and the outer concentric boom provides for radial addition of compressed air to complete combustion. Each boom is constructed of 304 stainless steel and is water-cooled. Figure 2 presents a schematic of the facility with the reburning booms installed at nominal locations.

For this test series a Number 2 distillate oil and a Number 5 heavy oil were fired in the primary burner. Ammonia-doped and undoped natural gas was used as the reburning fuel to vary fuel nitrogen content. Total boiler load was held constant during the reburning tests, requiring that, as secondary load increased, main burner load decreased. Testing consisted of measuring stack exhaust emissions (O_2, CO_2, CO, and NO) for several single parameter variation test series. The NO_x monitor used was a TECO Model 10A chemiluminescence analyzer.

RESULTS AND DISCUSSION

As discussed in the following paragraphs, baseline (without reburning) and parametric tests were conducted to characterize reburning applied to a commercial firetube package boiler. Overall reburning NO_x reductions of 50 percent and more were achieved with the optimization of a variety of process parameters, as discussed in the example that concludes this discussion.

Baseline Tests

Baseline testing consisted of measuring the exhaust NO_x emission, centerline temperature profile, and visible flame length as a function of main burner firing rate for both distillate and heavy fuel oils. Exhaust NO_x concentration, measured on a dry basis and corrected to zero percent O_2, is presented in Figure 3 as a function of the percent of full load. The full load NO_x emission level for the distillate oil (containing 0.01 percent nitrogen) is approximately 85 ppm; for the heavy fuel oil (containing 0.14 percent nitrogen) the full load emission is 200 ppm. From Figure 3 it is observed that exhaust NO_x emissions decrease between 5 and 10 percent as primary load is dropped. This is characteristic of many applications where burner derating results in reduced flame zone mixing intensities and, hence, reduced NO_x.

With a practical burner, there is no well defined flame shape. Primary flame length fluctuations of up to 0.5 m (1.6 ft) were observed. The average flame length decreased noticeably with decreasing load, from 2.5 m (8.2 ft) at full load to 1.5 m (4.9 ft) at 75 percent of full load. The reduced primary flame length allows for secondary fuel injection near the end of the visible flame with sufficient boiler length remaining for reburning. Figure 4 presents axial temperature profiles as measured on the boiler centerline for the heavy fuel oil. Temperatures were measured with a suction pyrometer at 25 cm (10 in) intervals, with profiles recorded at five different firing rates. At the nominal secondary fuel injection point the centerline baseline temperature is about 1500 K (2290°F). Tests on the research boiler simulator indicate that, at this temperature, oil reburning leads to soot deposition on the water-cooled booms and on the boiler walls. Reburning in thermal environments less than 1600 K (2420°F) should be restricted to gaseous fuels.

Based on baseline tests, nominal operating conditions were defined. Heavy fuel oil was chosen as the nominal primary fuel because it provides an initial NO_x level comparable to the nominal primary NO_x concentration used in PBS testing. A nominal secondary fuel injection location of 1.52 m (60 in) was defined based on flame length and temperature measurements. The final air injection location was selected to be 2.13 m (84 in), providing a rich zone bulk residence time of approximately 200 ms.

Reburning Tests

Single parameter variation tests were conducted on the major reburning process variables, including stoichiometry, initial NO_x, reburn fuel nitrogen, and residence time. Baseline tests (without reburning) were conducted prior to and at the conclusion of each test series to define primary zone effluent composition.

Initial NO and Rich Zone Stoichiometry. Figure 5 presents plots of reburn efficiency versus rich zone stoichiometry when firing No. 2 and No. 5 fuel oils in the main burner. The fraction of total boiler load contributed by the secondary fuel is shown as an alternate abscissa. Reburn efficiency is defined as the ratio of the exhaust NO emission with reburning to the primary NO_x emission at the reduced primary load. When compared to data obtained from PBS reburning tests under similar conditions, agreement is observed within the indicated data uncertainty bands.

Tests have been performed wherein the secondary fuel injection patterns were varied. Included were trials where the secondary fuel was (1) injected radially outward from the centerline boom assembly, (2) injected circumferentially near the firetube wall, and (3) injected in a manner to achieve a spatially uniform distribution of stoichiometry. For this broad variation in mode of secondary fuel addition, there was essentially no variation in the extent of NO_x emission reduction by reburning [6]. This observation, which requires experimental verification to be extrapolated to other boiler types, significantly simplifies the design of reburning retrofit hardware for the firetube package boiler class.

As rich zone stoichiometry decreases, two factors contribute to improved NO reduction. First, the availability of more hydrocarbon radicals results in increased destruction of primary NO. Second, a larger portion of the fuel is consumed in an environment not conducive to NO formation. Thus, the low-NO_x secondary burner heat release "dilutes" the relatively high NO_x primary burner effluent. This dilution component is strongly coupled to the destruction component of NO_x reduction and cannot be straightforwardly isolated.

Clearly, initial NO_x concentration influences the degree of NO_x reduction under a given set of reburning conditions. North American boiler tests yielded significantly smaller reductions for the low initial NO_x condition than for the high initial NO_x condition. For the distillate primary fuel condition (initial NO_x of 80 ppm), with 20 percent of the total load used for reburning, primary NO_x is reduced by about 20 percent; for the heavy fuel oil condition (initial NO_x of 180 ppm), a 40 percent reduction is realized under the same conditions. From results of PBS testing where initial NO_x concentrations were varied from 50 to 500 ppm, reaction orders with respect to NO_x between 1.5 and 1.6 were calculated for rich zone stoichiometries between 1.0 and 0.8. This contradicts the first order reduction claims of the MHI investigators [5]. It is concluded here that, for low initial NO_x values (less than 200 ppm), other process parameters beside rich zone stoichiometry must be optimized to achieve 50 percent NO_x reductions.

Reburn Fuel Nitrogen. When ammonia is doped into the secondary natural gas stream, NO reductions are decreased sharply. Figure 6 shows this data trend for ammonia doping of up to 1 percent. Though not directly comparable to fuels containing nitrogen (doping with a cyano compound like hydrogen cyanide would more closely model fuel-bound nitrogen evolution, but would also present increased safety hazards), these tests indicate that fuel nitrogen is an important factor in the reburning mechanism.

Rich Zone Residence Time. Reburn zone length was varied from 0.3 to 0.6 m (1 to 2 ft) by shifting the location of the final-air injection. Injecting the final air beyond 2.13 m (84 in) resulted in burnout zone residence times too short to achieve sufficient fuel burnout prior to thermal quenching, resulting in high CO stack emissions. Figure 7 shows that the limited residence time data obtained agree well with PBS results under similar test conditions. Detailed measurements in the PBS facility indicate that the characteristic kinetic time necessary for the rich zone species to approach an equilibrium is 50 ms. For a bulk residence time of 200 ms, the highest velocity rich zone streamtube has a rich zone residence time of 50 ms. Geometrically similar to the PBS facility, it is suggested that a rich zone bulk residence time of approximately 200 ms represents a near-optimum reburn zone length in the North American boiler.

Example

To put the above factors into perspective, an example is presented to show how reburning might be applied to achieve a significant level of NO_x emission reduction. This example is presented schematically as Figure 8. The initial condition selected is full-load operation firing Number 5 fuel oil at 15 percent excess air. The NO_x emission level at that condition is 233 ppm. The first step is to reduce the primary flame excess air from 15 to 10 percent. This reduces the exhaust NO_x emission level to 200 ppm. Next, the boiler load is reduced by 15 percent, holding excess air constant at 10 percent. This reduces the NO_x emission level to 168 ppm. Third, secondary flow of natural gas and final air is initiated to return the boiler to full load with a stack excess air of 10 percent. Accomplishing the third step sets the fuel-rich zone stoichiometry at 0.94. This causes the exhaust NO_x emission level to drop to 113 ppm. To return the overall excess air to 15 percent, the final air flow rate is increased, causing the exhaust NO_x emission level to increase to 115 ppm.

In this example, overall NO_x reduction via reburning is achieved by means of primary load reduction, primary excess air reduction, and the destruction and dilution effects of staged fuel combustion. The example illustrates a net 50 percent reduction in NO_x achievable by reburning, precisely the reduction claimed by Mitsubishi in [5]. It is noted that the 50 percent NO_x reduction is achieved by diverting only 15 percent of the main burner load and that larger emission reductions are possible. This should result from further process optimization.

SUMMARY

The results from the reburning application tests are summarized in the following two conclusions:

- o NO_x reductions of 50 percent and greater are achievable with the application of reburning to firetube package boilers.
- o Retrofit modifications for natural gas reburning require minimal cost and effort.

The input/output demonstration tests provide little insight into the chemistry and physics of reburning, but do verify results obtained from the fundamental PBS tests. Future testing will focus on the application of oil reburning to firetube package boilers.

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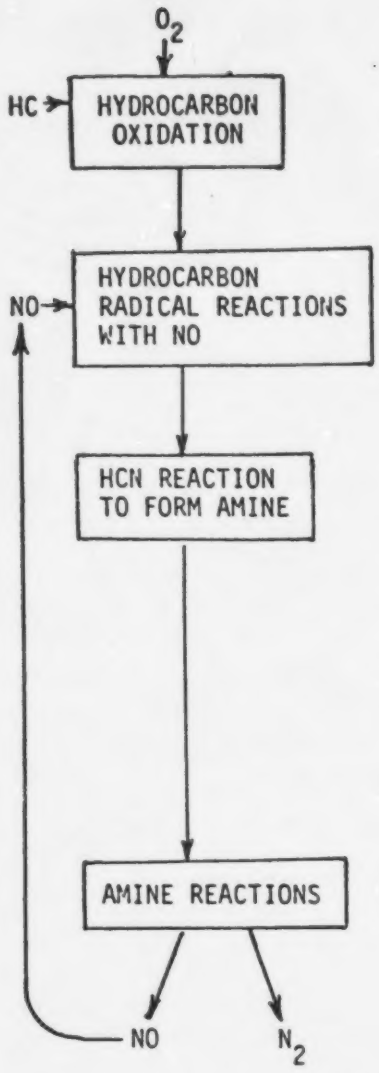

$$CH_4 + O_2 \longrightarrow CH_3 + OH$$

$$CH + NO \rightarrow HCN + O$$

$$HCN \xrightarrow{OH} CNO \xrightarrow{H} NH$$

OR

$$HCN \xrightarrow{O} NH$$

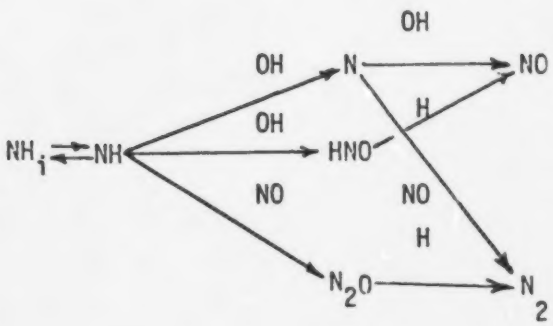

Figure 1: Chemical Mechanism for NO_x Destruction by Hydrocarbons

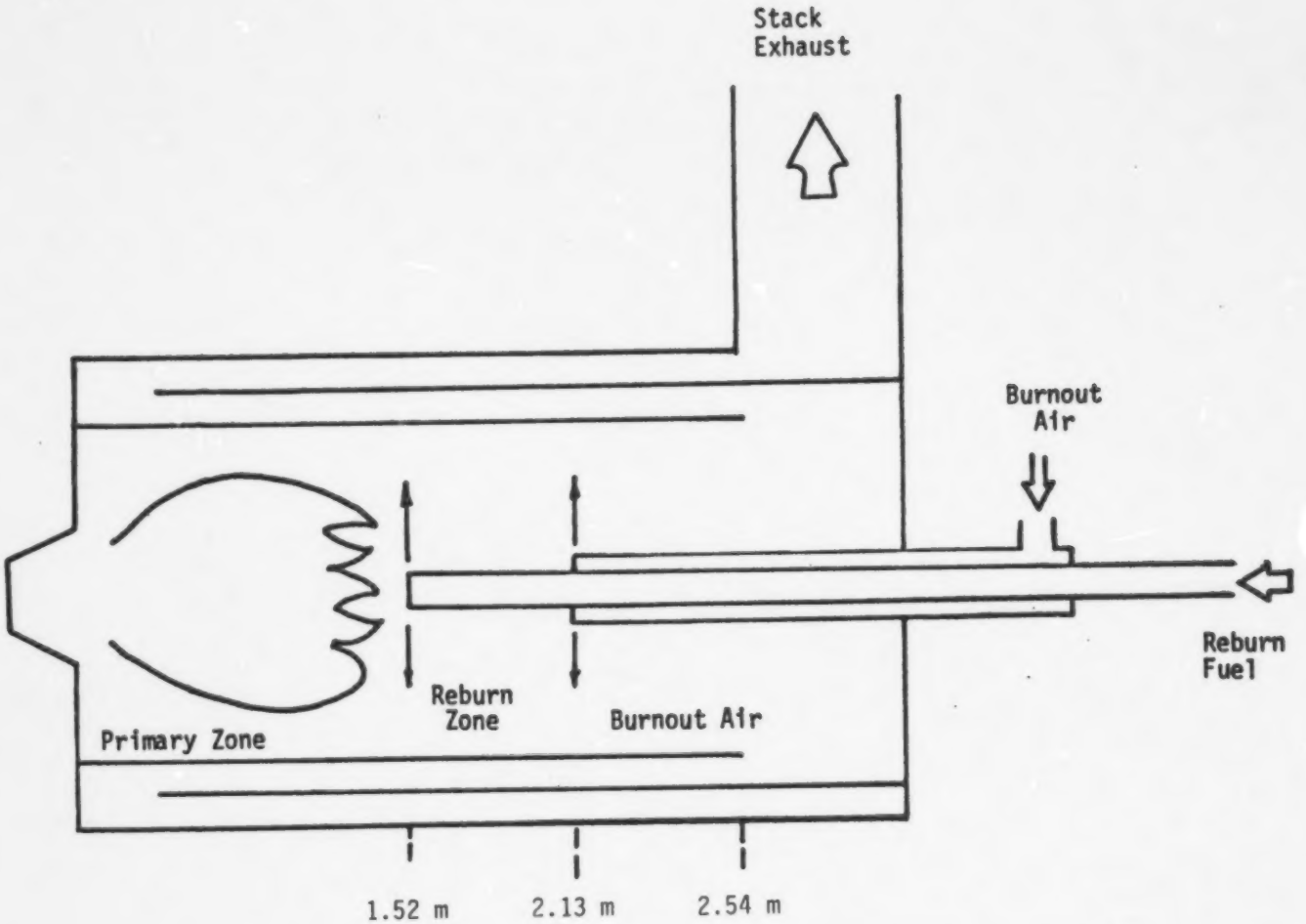

Figure 2: North American Boiler

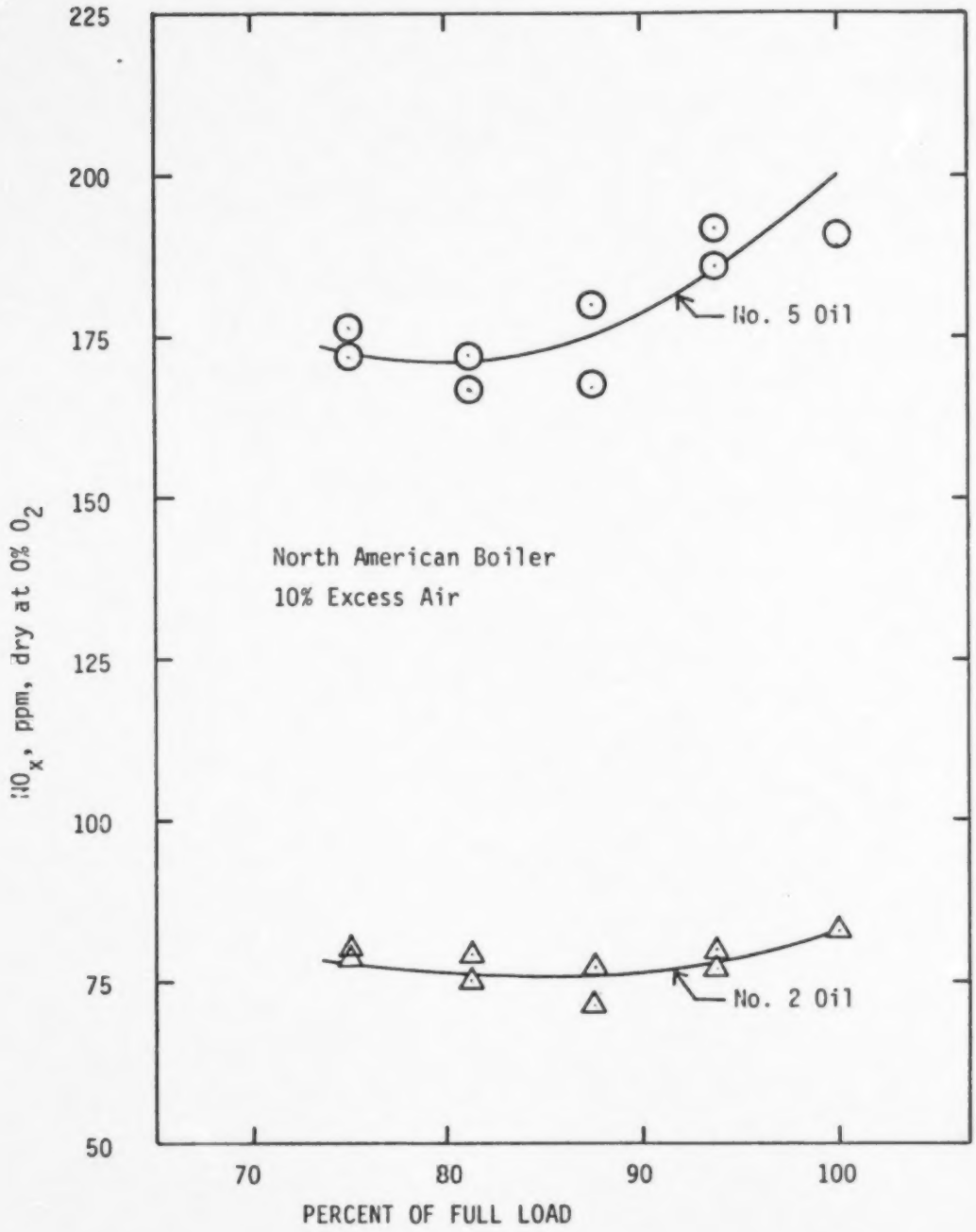

Figure 3: Exhaust NO_x Versus Primary Burner Firing Rate

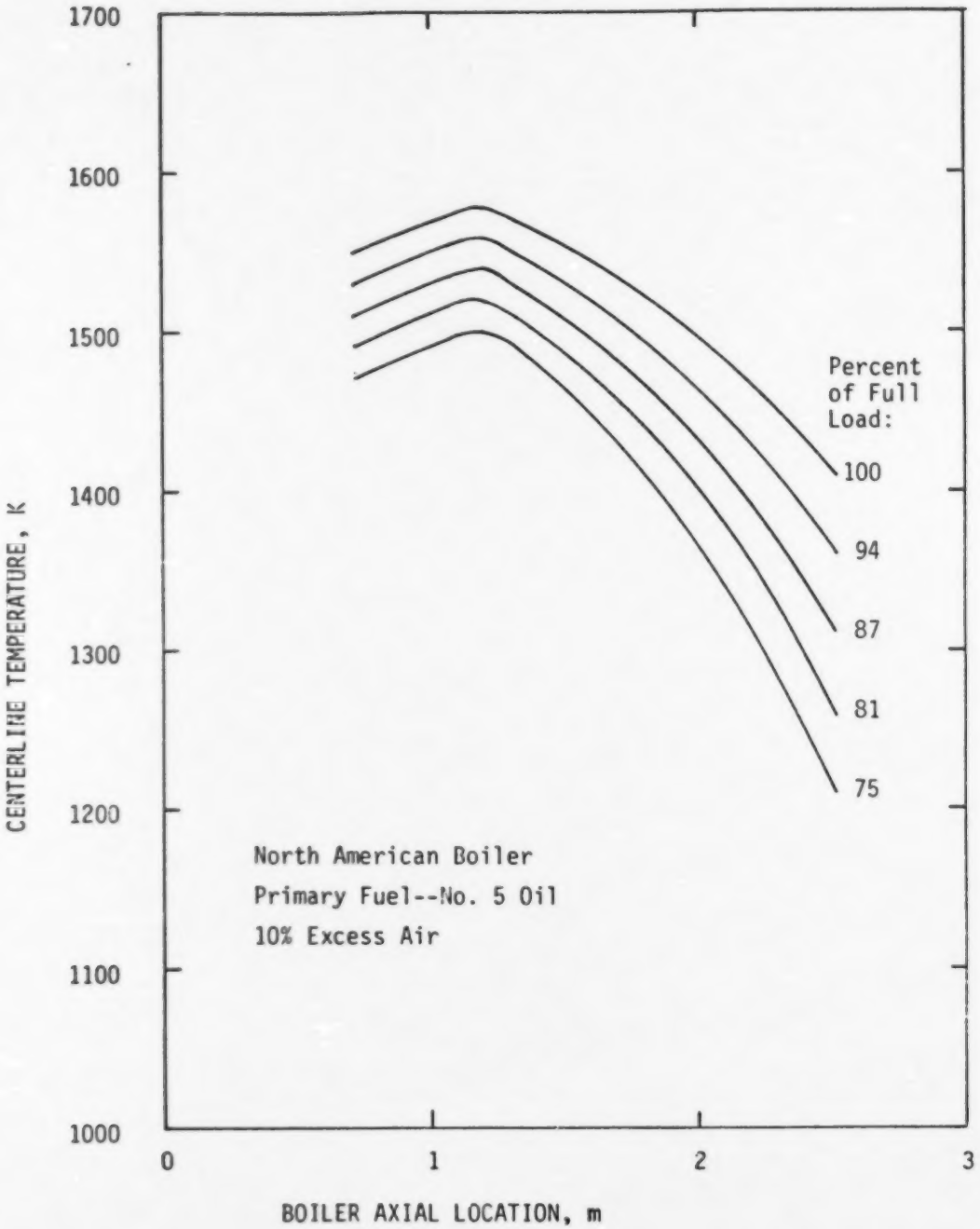

Figure 4: Centerline Temperature Profile for Heavy Oil Firing

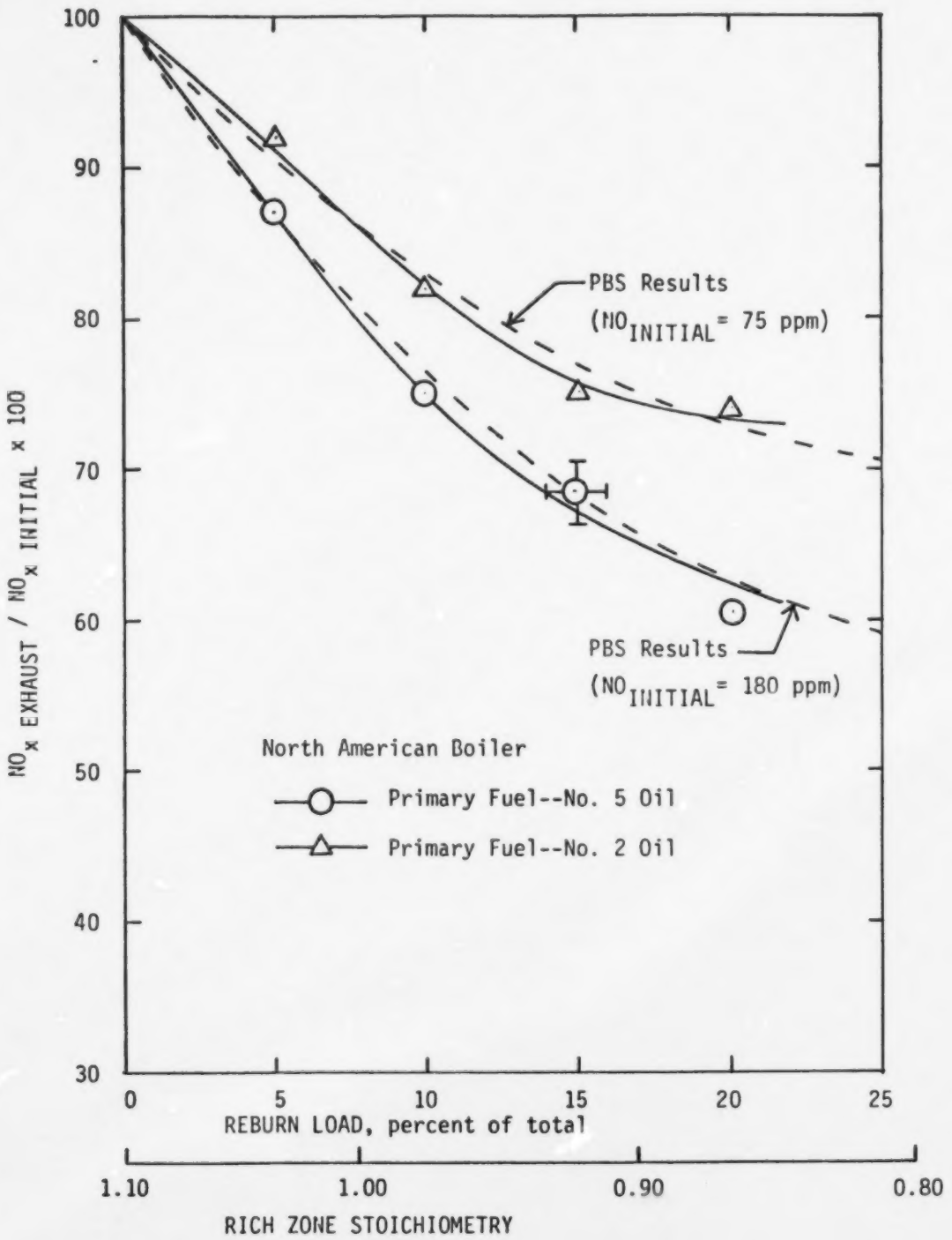

Figure 5: Natural Gas Reburning in the North American Boiler

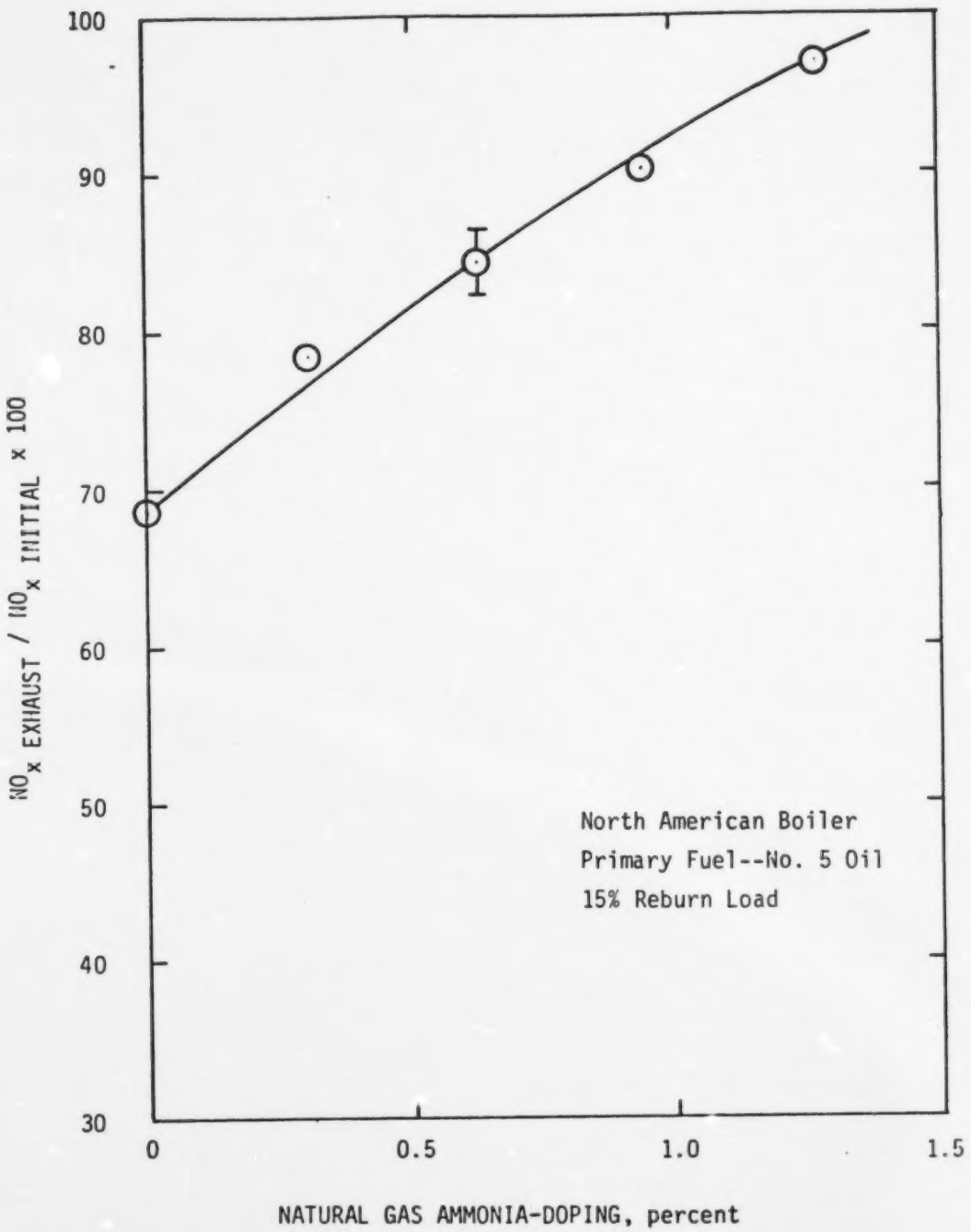

Figure 6: Reburn Efficiency Versus Amount of NH_3-Doping of Secondary Fuel

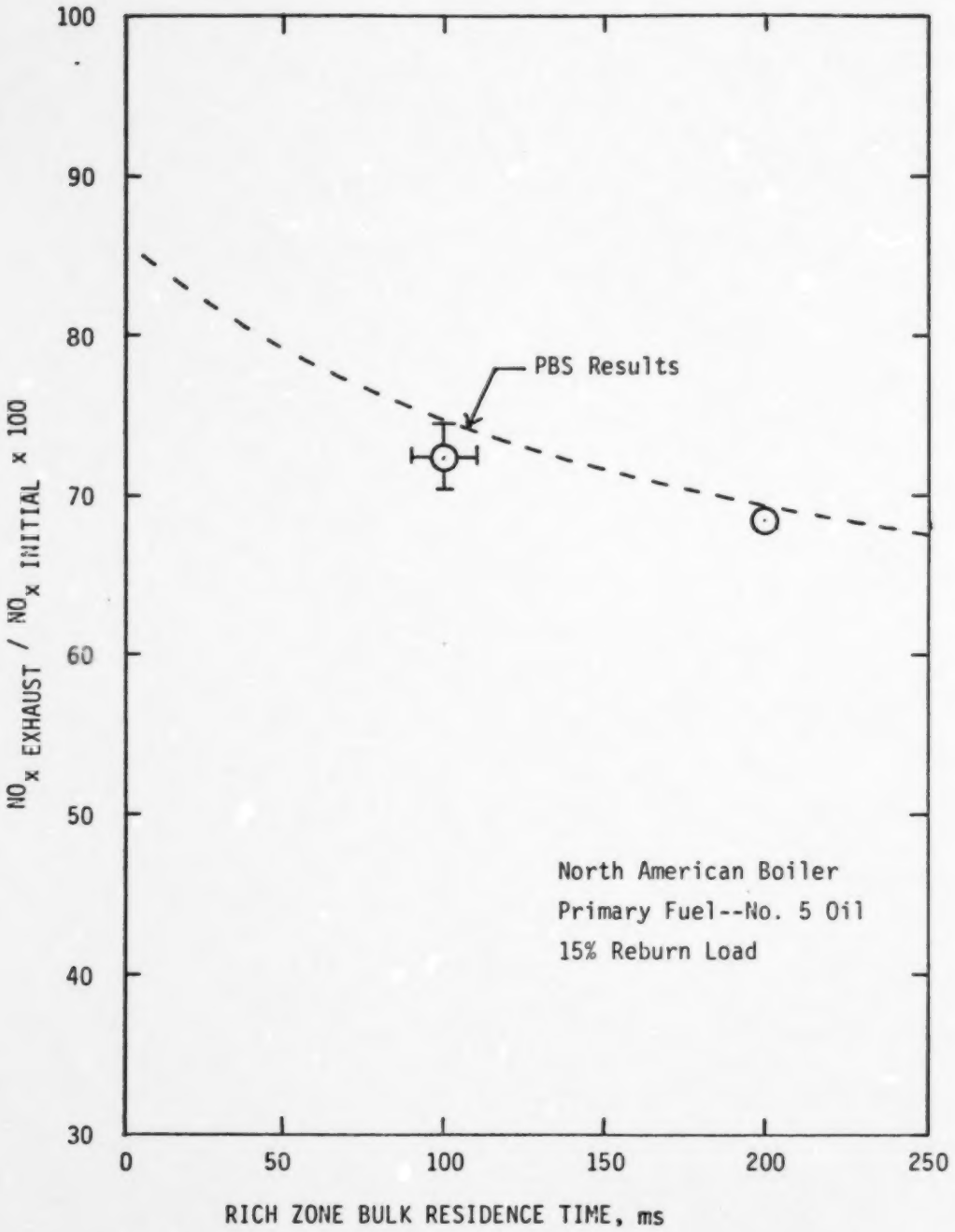

Figure 7: Reburn Efficiency Versus Rich Zone Residence Time

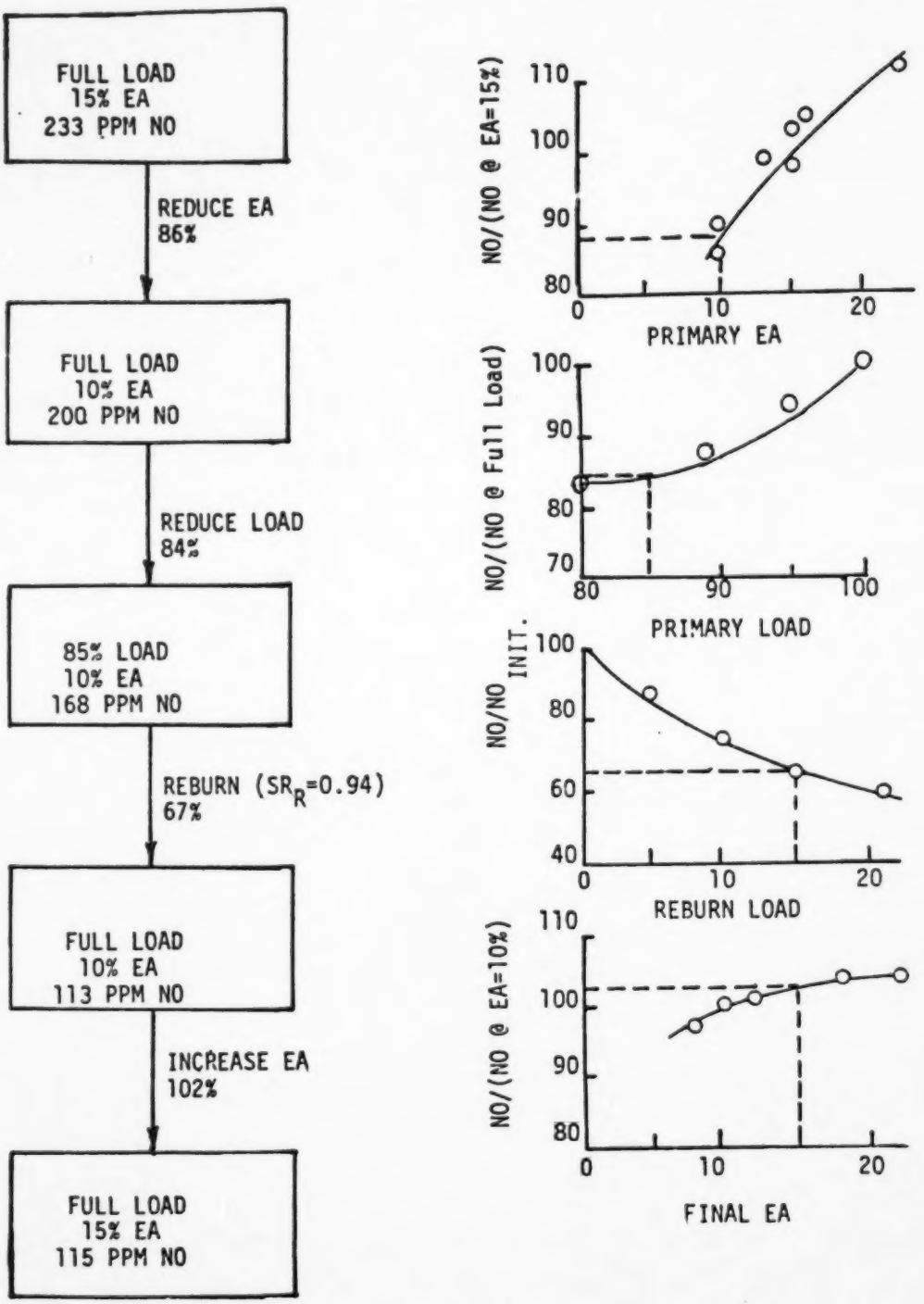

Figure 8: North American Boiler Reburning Example